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Kinetics of solid-liquid-liquid oxidation of 4-Methylanisole to p-anisaldehyde

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1. Introduction:

Oxidation of aromatic compounds produces chemicals and intermediates useful in pharmaceuticals and perfumery [1]. Liquid-phase oxidation is preferred over gas-phase oxidation due to its compact nature. The product of liquid-phase oxidation of substituted toluene is usually aldehyde. The aldehyde so formed has a tendency to get oxidized further to acid [2]. Moreover, the mechanisms of such reactions are challenging due to the possibility of parallel and consecutive paths, which lead to byproduct generation [3]. Here, we have studied the liquid phase oxidation of 4-Methylanisole to p-anisaldehyde using MnO_2 as an oxidant. p-anisaldehyde is an important chemical for industries like perfumery, fragrance, pharmaceuticals and agrochemicals.

2. Material and Methods:

2.1 Material: 4-Methylanisole, MnO_2, sulfuric acid (98%) and methanol for HPLC

2.2 Methodology: The glass reactor with baffles was charged with reaction mixture. A pitched-blade turbine impeller along with overhead stirrer and the thermostat were used. The reaction was carried out at optimized parameters. The reaction mixture was finally quenched, and both the organic and aqueous phases were separated and analyzed with HPLC.

2.3 Characterization: The average particle size of MnO_2 powder was 1.69µm. The XRD analysis of MnO_2 was carried out to determine its crystal structure.

3. Significant Results and Discussion

3.1 Reaction Mechanism: The reaction mechanism pathway is not very well explained in the literature. The interaction between mass transfer and chemical reactions was investigated for the plausible mechanisms.

3.2 Analysis of mass transfer effects: The agitation showed a strong effect on the rate of reaction, thereby influencing the mass transfer coefficient and interfacial area. Moreover, the substantial effect of agitation on the rate of reaction was also supported by the correlations used.

3.3 Reactions conditions effect: The effects of parameters such as agitation, temperature, substrate concentration, sulfuric acid concentration and solid loading were examined for the 4-Methylanisole oxidation. The overall order of the reaction was first with respect to 4-Methylanisole.The apparent activation energy of the reaction was 13kcal/mol. The activation energy indicated an intermediate control regime for the reaction.

3.4 Variation in moles of reactant, product and byproduct over time: The variation in moles of reactant, product, and byproduct over time was studied at 200 rpm and 25°C up to 12 hr and depicted in Figure1. 4-Methylanisole moles decreased with time as the reaction progressed, while product of reaction, p-anisaldehyde moles increased over time. The increment in the byproduct, i.e., anisic acid moles, with time was found to be very low. It is due to further oxidation of product reducing its selectivity.

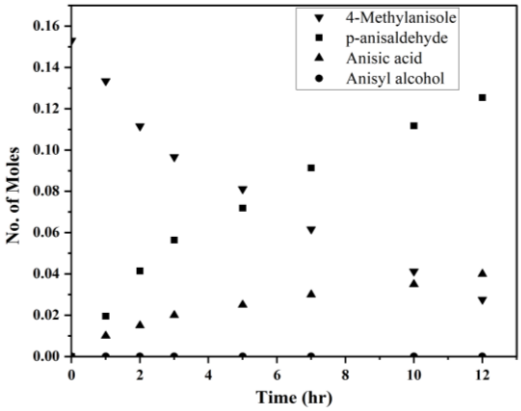

Figure 1: The variation in moles of reactant, product and byproduct over time

3 Conclusions:

The engineering aspects of the kinetics of the selective oxidation of 4-Methylanisole to p-anisaldehyde were studied. The reaction occurred via a radical intermediate mechanism. A model was developed incorporating the interplay between mass transfer and chemical reaction and thus the overall impact, which will help in the scale-up. The overall 81% conversion of 4-Methylanisole was achieved with a selectivity of around 75%.

References

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